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Theoretical Dissociation Energies for Ionic Molecules

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Abstract

Ab initio calculations at the self-consistent-field and singles plus doubles configuration-interaction level are used to determine accurate spectroscopic parameters (D_e , r_e , ω_e) for most of the alkali and alkaline-earth fluorides, chlorides, oxides, sulfides, hydroxides and isocyanides. Numerical Hartree-Fock (NHF) calculations are performed on selected systems to ensure that the extended Slater basis sets employed for the diatomic systems are near the Hartree-Fock limit. Extended gaussian basis sets of at least triple-zeta plus double polarization quality are employed for the triatomic systems. By dissociating to the ionic limits, most of the differential correlation effects can be embedded in the accurate experimental electron affinities and ionization potentials. With this model, correlation effects are relatively small (0.0-0.3 eV), but invariably increase D_e . The importance of correlating the electrons on both the anion and the metal is discussed.

The theoretical dissociation energies (D_e) are critically compared with the literature to rule out disparate experimental values. The theoretical studies combined with the experimental literature allow us to recommend D_e values that are accurate to 0.1 eV for all systems considered. The systematic treatment of many different systems reveal many trends. For example, the dissociation energies of the alkali and alkaline-earth hydroxides are observed to be less than the corresponding fluorides by just slightly less than the difference in electron affinities of F and OH. In general, there is a strong correlation between the dissociation energy (to ions) and r_e , because the bonding is predominantly electrostatic in origin.

Theoretical $^2\Pi - ^2\Sigma^+$ energy separations are presented for the alkali oxides and sulfides. The ground states of all the alkali sulfides are shown to be $X^2\Pi$. An extensive study of the $^2\Pi - ^2\Sigma^+$ energy separation in KO reveals a $^2\Sigma^+$ ground state at all levels of theory. The separation is shown to be sensitive to basis set quality, and in the NHF limit the $^2\Sigma^+$ state is lower by about 250 cm^{-1} . The separation is almost unaffected when the 16 valence electrons are correlated at the singles plus doubles level using an extended Slater basis.

I. Introduction

The dissociation energies (D_0) of many of the ionic molecules containing the alkali and alkaline-earth atoms have been determined experimentally. The dissociation energies of the alkali halides reported by Brewer and Brackett [1] in 1961 are still accepted today. Their dissociation energies are limited in accuracy only by the quality of the initial vapor pressure data and by the necessary corrections for gaseous imperfection. In contrast, experimental dissociation energies for the alkaline-earth oxides show a wide variation. For MgO, the experimental D_0 values [2-7] range from 3.5-4.3 eV, whereas a recent theoretical study [8] obtains 2.65 ± 0.16 eV. For CaO, two chemiluminescence studies yielded disparate D_0 values of $(\geq 4.76 \pm 0.15$ eV [9] and 4.11 ± 0.07 eV [10]. Theoretical studies [11] gave excellent agreement with the lower value, supporting Dagdigian's conclusion that the higher value was incorrect as a result of interference with CaCl [10].

It is demonstrated in this paper that theoretical dissociation energies can be computed with 0.1 eV accuracy for large classes of ionic diatomic and triatomic systems. Considered herein are most of the alkali and alkaline-earth fluorides, chlorides, oxides, sulfides, hydroxides and isocyanides. The theoretical dissociation energies are capable of ruling out disparate experimental values, and allow an overall assessment of the various experimental methods used to determine dissociation energies. Our theoretical methods described in detail in the next Section reflect the fact that the charge distribution in ionic molecular systems much more closely resembles the constituent ions than the neutrals. Hence, by dissociating to the ionic limits and then correcting to the neutral limits using the accurate experimental ionization potentials and electron affinities, the problem can be formulated such that relativistic and correlation contributions to the dissociation energies are relatively small (≤ 0.3 eV). This is documented for a large number of systems by comparing self-consistent-field (SCF) and singles plus doubles configuration-interaction, CI(SD), values for D_0 .

For the alkali oxides and sulfides we have considered both the lowest $^2\Sigma^+$ and $^2\Pi$ states. This is of particular interest for the alkali oxides, where there is a change in ground-state symmetry from LiO($^2\Pi$) to CsO($^2\Sigma^+$). For the KO molecule there is both conflicting experimental [12-13] and theoretical [14-15]

evidence for the ground-state symmetry. This work provides rather strong support for KO($X^2\Sigma^-$). In contrast, the alkali sulfides Li-Rb are shown to have $X^2\Pi$ ground states, probably as a result of the increased bond lengths.

I. Methods

The fraction (f) of ionic character in a bond is difficult to quantify. Pauling's criterion [16], $f = \mu/e r_e$, where μ is the dipole moment and r_e is the equilibrium internuclear separation is not a good measure of ionicity in highly ionic systems owing to the large deformations caused by the electrostatic field of the ions. Although Mulliken populations can show ionic character, they are difficult to quantify and often vary significantly with the one-particle basis (e. g. diffuse functions increase the overlap population which is difficult to assign). The best measure of ionic character is probably the ratio r_x/r_e where r_x is the hypothetical crossing point where a purely ionic potential curve crosses the asymptote of the covalent curve. In Table I we have tabulated this ratio for selected alkali and alkaline-earth fluorides, chlorides, oxides and sulfides. Systems for which $r_x/r_e \leq 2.5$ potentially have some covalent character in the bond. By this criterion, all of the alkali and alkaline-earth oxides and sulfides as well as the alkaline-earth halides of Be and Mg could contain some covalent character.

For highly ionic systems, such as the alkali halides, the molecules can be considered to be composed of ions, each of which is polarized by the electrostatic field of the other. For these systems most of the binding energy arises from purely electrostatic interactions between the ions: charge-charge interaction, charge-dipole interaction, dipole-dipole interaction, and quasi-elastic energy stored in the induced dipoles. According to the Rittner model [17], this portion of the binding (ϕ) can be expressed in terms of the atomic polarizabilities (α_1 and α_2) as

$$\phi = \frac{-e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{2r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} \quad (1)$$

The Rittner model has yielded reliable binding energies for the alkali halides where accurate experimental r_e values are available. In addition, the model of Kim and Gordon [18] for describing forces between closed-shell atoms has been successfully applied to the alkali halides.

Probably the most rigorous theoretical treatment of the dissociation energies

(D_e) of selected alkali halide molecules is given in a series of papers by Matcha [19]. He computed D_e at the SCF level with large Slater bases, and then corrected for correlation and relativistic effects using atomic data. In his formalism the total dissociation energy of the molecular system MX is given by $D_e = D_e^{\text{HF}} + D_e^{\text{corr}} + D_e^{\text{rel}}$ where

$$D_e^{\text{corr}} \approx E_M^{\text{corr}} + E_X^{\text{corr}} - E_{M^+}^{\text{corr}} - E_{X^-}^{\text{corr}} \quad (2)$$

and

$$D_e^{\text{rel}} \approx E_M^{\text{rel}} + E_X^{\text{rel}} - E_{M^+}^{\text{rel}} - E_{X^-}^{\text{rel}} \quad (3)$$

Formulated in this way D_e^{corr} is positive and can be quite large. Matcha obtained rather good agreement with the available thermochemical D_o . His values are slightly low because his basis sets were still not at the HF limit, and he neglected the inter-fragment correlation energy (see later discussion).

The formalism that we employ herein is essentially equivalent to Matcha's, but avoids explicitly knowing the total correlation and relativistic energies of the atoms and corresponding ions. Also, our approach includes the interfragment correlation which, although small in total energy (e. g. 0.18 eV for NaF), is entirely differential since it vanishes in the asymptotic limit. The dissociation energy of MX can be written as

$$D_e = E(M^+) + E(X^-) - E(MX, r_e) - IP(M) + EA(X) \quad (4)$$

Hence, we explicitly dissociate to the ionic limits and then correct to the neutral ground state atomic limits using the accurate experimental ionization potentials (IP) available from Moore [20], and electron affinities (EA) available from Hotop and Lineberger [21]. Since most of the differential correlation and relativistic effects are absorbed into the IP and EA, the SCF dissociation energies, D_e^{SCF} , are potentially quite accurate. Note that it is necessary to apply this formalism to a molecular state that is well represented by the HF configuration. This is true of the ground states of all of the systems considered herein except for the alkaline-earth oxides and sulfides whose ${}^1\Sigma^+$ ground states require a multireference description owing to the fact that they are a mixture of singly and doubly ionized structures. Hence, for these systems we have applied our formalism to either the excited

a³Π or A¹Π states, both of which are well described by a single reference configuration. The ground-state D_e can then be computed if the T_e is known for the excited state.

For the formalism in Eq. 4 to be accurate, the basis sets must approach HF quality. Since the atoms approach the HF limit much more quickly than the molecular systems, the D_e^{SCF} values almost invariably increase monotonically with improvements in basis set quality. For all of the diatomics considered herein, we have employed extended Slater bases. They begin with the accurate sets of Clementi and Roetti [22] and were modified slightly where necessary to reduce problems with linear dependency. The basis sets are then further augmented with polarization functions to describe the considerable distortions that arise in the field of the ions. These basis sets are described briefly in Table II. Additional details can be found in forthcoming publications [23-28]. To assess how close our SCF energies are to the HF limit, we have considered two approaches. First, for the lighter molecular systems (e.g. NaF, NaO, KO and BeCl) we have carried out numerical Hartree-Fock (NHF) calculations using an implementation of McCullough's numerical diatomic code [29] on the Cray XMP. The numerical calculations show that our Slater bases are very near the HF limit (error < 0.02 eV). For the heavier systems such as SrO, we have used basis set saturation studies to assess the degree of basis set incompleteness. Here the error is somewhat larger (0.20 to 0.25 eV), but most of the loss is in the core, so that our D_e^{SCF} is only low by about 0.07 eV. Also, for the triatomic systems considered herein, we have used extended gaussian basis sets, so again there is a tendency for our D_e^{SCF} values to be slightly low.

Since near HF quality D_e values can be produced using the formalism in Eq. 4, the question naturally arises as to how well these D_e^{HF} reproduce the true values. In other words, the D_e^{HF} will be accurate if the two conditions

$$E_{\text{MX}}^{\text{corr}} \approx E_{\text{M}^+}^{\text{corr}} + E_{\text{X}^-}^{\text{corr}} \quad (5)$$

and

$$E_{\text{MX}}^{\text{rel}} \approx E_{\text{M}^+}^{\text{rel}} + E_{\text{X}^-}^{\text{rel}} \quad (6)$$

are satisfied. The second condition is expected to be well satisfied for all systems considered herein, since only the valence electrons are substantially distorted by the electrostatic field. We have examined the approximation in (5) by performing

singles plus double configuration-interaction, CI(SD), calculations from the SCF reference configuration for all systems as well as more restricted CI calculations for selected systems. We find, invariably, that correlation increases the dissociation energies, making the D_e^{HF} lower bounds. Also, since $E_{\text{diff}}^{\text{corr}}$ is always quite small (0.0-0.3 eV) the SCF model as used in Eq. (4) is a good approximation to D_e . Apparently, SCF calculations using extended basis sets accurately portray the charge distribution in these ionic molecules near their equilibrium geometry.

In all CI calculations we correlate the n and (n-1) shells on the alkali and alkaline-earth cations, which includes the 1s electrons for Li and Be. The outermost seven valence electrons are correlated for the oxide and sulfide anions, and the outermost eight valence electrons are correlated for the fluoride, chloride, hydroxide and isocyanide anions. Hence, for example, 17 electrons are correlated for the alkaline-earth halides, except for Be where 11 electrons are correlated. When this many valence electrons are correlated, one must potentially contend with size consistency, basis set incompleteness, and basis set superposition errors, especially considering the small differential correlation contribution to D_e .

To facilitate the discussion of electron correlation let us divide the configuration-state functions (CSFs) into three classes. Class 1 and 2 contain all single and double excitations from the orbitals that can be identified as X^- and M^+ , respectively. Class 3 contains the important pair-pair terms, which are the double excitations where one electron is excited from an M^+ orbital and the other from an X^- orbital. This third class is size consistent, since it contributes nothing at infinite separation, but increases in importance as the bond distance decreases.

If only class 1 CSFs are included, the calculation is size consistent, but the energy is not invariant to a unitary transformation among the M^+ and X^- occupied orbitals. For example, accidental degeneracies between the M^+ and X^- orbitals result in arbitrary mixings that tend to reduce the correlation energy of both the alkali oxides and fluorides. Hence when the electrons on only one center are correlated, we use corresponding orbitals [30] to rotate the orbitals to give maximum overlap with the M^+ orbitals. If the orbitals are not rotated, then the effect of the class 1 CSFs, which is to decrease D_e and ω_e and to increase r_e , can be significantly accentuated. If only the class 1 CSFs are included, then the resulting spectroscopic constants (D_e, r_e, ω_e) are in worse agreement with experiment than are

the HF values. These comments are illustrated by the CI results for the $^2\Sigma^+$ ground state of NaF in Table III. If only the eight valence electrons on F^- are correlated, D_e is reduced by 0.08 eV, and by an even larger amount if the orbitals are not first localized. Also, r_e increases by 0.02 Å worsening the agreement with experiment. In contrast, correlating the eight valence electrons on Na has little effect on D_e or r_e , which is not surprising considering the compact nature of the Na^+ orbitals.

The class 3 excitations (pair-pair terms) have an opposite and somewhat larger differential effect than the class 1 excitations. Hence, including both classes (still size consistent) tends to increase D_e and ω_e slightly, and to decrease r_e , resulting in better agreement with experiment, particularly for the heavier alkali and alkaline-earths. The sum of the three disjoint classes, which contains all of the CSFs in the full CI(SD), should approximate the full calculation. In practice, the sum is a slight over-estimation of the combined effect, because the importance of the pair-pair terms (class 3) is reduced somewhat in the full calculation. The fact that the effect of the three classes is nearly additive suggest that the calculations are nearly size consistent if compared with the supermolecule. One can also rationalize the absence of any significant size-consistency error based on the small differential correlation energy observed. This is further supported by the fact that corrections for higher excitations using either the Davidson's formula [31] or CEPA1 [32] have negligible effect on the computed D_e . The energy of the supermolecule was based on a point computed at an internuclear separation of at least 20 Bohr. Note that there is a rather large size-consistency error (≈ 0.5 eV) if the calculations are referenced to the sum of the ions.

Another potential problem that arises in the CI calculations is basis set superposition errors. At this level of correlation treatment, significant demands are put on the quality of the basis set. For example, it is necessary to have sufficiently tight polarization functions to correlate the contracted spatial distribution of the occupied orbitals on M^+ . We have computed the basis set superposition errors in our large CI calculations using the counterpoise method. This approach is an upper bound to the error, since the counterpoise method tends to overestimate the superposition error, especially if the occupied space of the ghost atom is not excluded. The absence of a single basis function (such as a compact 3d function on M) can result in several tenths of an eV superposition error, and artificially

increase the calculated D_e . These statements are well illustrated by the following example for CaF. If we use three Slater 3d functions for Ca atom ($\alpha=4.76666, 2.1222, 0.8007$) we find essentially no basis set superposition error at the SCF level, but a 0.129 eV error at the CI(SD) level when the fluorine ghost basis is brought up to 3.7 Bohr. When the Slater 3d basis is expanded to four Slater functions ($\alpha=6.0, 3.0, 1.5, 0.75$) this error is reduced to 0.029 eV, and further to 0.014 eV when the occupied fluorine orbitals are excluded. Reducing the superposition error by 0.10 eV decreased the dissociation energy by 0.08 eV and increased r_e by 0.012 Å. Using the counterpoise method, we observe a 0.035 eV superposition error for fluorine in the presence of the Ca basis (0.030 eV with the calcium occupied space deleted). Hence, with the larger CaF basis, the total superposition error is about 0.05 eV at the CI(SD) level. Based upon tests for several systems, we believe our basis set superposition errors are less than 0.1 eV and, to a large extent, are cancelled by basis set incompleteness. However, this example illustrates the necessity of using very complete basis sets at the CI(SD) level to keep basis set superposition errors below the small differential correlation effect on D_e .

In performing our CI(SD) calculations from the SCF reference configuration for open shells, we generally invoked the interacting space [33], i.e. only those double excitations that have non-zero matrix elements with the SCF reference configuration are included. This has a small effect on the total energy, but essentially no effect on the spectroscopic parameters. Although, in general, we included all virtual orbitals in the CI, our results indicate that eliminating the high-energy virtuals (core correlating orbitals) also has very little effect on the spectroscopic parameters. We also find that the spectroscopic parameters are insensitive to corrections for higher excitations [31], which is not surprising, considering the small total CI effect observed. We have performed CEPA1 calculations [32] on several systems, but have not reported these results here since they are not significantly different from the CI(SD) values.

The initial phase of the study was done on the Cray-XMP using the DERIC-SWEDEN or MOLECULE-SWEDEN [34] molecular structure codes. When the Cyber-205 became available at NASA-Ames, we began calculations using the Karlsruhe adaptation [35] of the COLUMBUS codes [36-39]. The Slater integrals were again evaluated with the diatomics integral program DERIC [40]. Extensive tests were performed to ensure that the two independent sets of programs gave

identical CI(SD) energies. More details of the program comparisons are given in the original papers [23-28].

III. Results and Discussion

Before proceeding with a discussion of the dissociation energies of the individual molecular systems, it is useful to discuss the overall trends that have been observed. In Fig. 1 we have plotted the dissociation energies, D_e , of the alkali and alkaline-earth fluorides, chlorides, oxides, sulfides and hydroxides with respect to ground state ions versus equilibrium bond length. The nearly linear relationship between bond length and D_e is striking. There is a tendency of the molecular systems containing Li and Be to fall above the curve, which probably arises from either the tendency of these systems to have a larger component of covalent character or the different core structure on the metal, i.e. s^2 versus $s^2 p^6$. The similarity of the fluorides and hydroxides is also quite evident from Fig. 1. Although the correlation diagram is not sufficiently accurate to predict D_e values, it is capable of ruling out widely divergent ones, such as all of the experimental values for MgO.

In the following Sections where we discuss the different classes of molecular systems, we present D_o values at both the SCF and CI(SD) level. In almost every case correlation acts to slightly increase D_o and decrease r_e , generally improving agreement with experiment. As discussed previously, the D_o^{SCF} are probably lower bounds, and the CI(SD) D_o are more likely low than high, especially for the heavier metals where we do not fully account for the bond contraction. We feel that all of the CI(SD) D_o values reported herein for the diatomic systems (except those involving Cs and Ba) are accurate to 0.1 eV. Our results on triatomic systems (hydroxides, isocyanides) that employ extended gaussian basis sets may be slightly less accurate, but again are more likely too low than high. Our theoretical results in conjunction with the available experimental values allow us to recommend reliable D_o values for all systems considered in this study.

This study also reports values for the spectroscopic parameters r_e and ω_e . The CI(SD) results are generally in excellent agreement with experiment, although there is a tendency for theory to obtain slightly long bond lengths for the heavier systems. Note that there is several thousands of an Angstrom uncertainty in the theoretical r_e values, and a much larger ($\approx 30 \text{ cm}^{-1}$) uncertainty in the ω_e values owing to the procedure of fitting the theoretical data to a parabola. In some instances we have done additional points on a tighter (0.05 Bohr) grid to stabilize

the ω_e values.

A. Alkali fluorides

Two complete sets of experimental D_o values exist for the alkali fluorides. Brewer and Brackett [1] determined D_o^{298} values using a third-law treatment of vapor pressure data combined with the enthalpies of formation of the solid alkali halides and the gaseous monatomic elements. Their experimental numbers are limited in accuracy by the original vapor-pressure data, and by the necessary corrections for gaseous imperfection. For an accurate comparison with our theoretical values given in Table IV, one should subtract 0.02-0.03 eV from their values to correct to absolute zero. The second set of experimental D_o values given in Table IV are the flame photometric values of Bulewicz et al [41]. These values are in substantial agreement with the thermochemical values, but contain a large uncertainty due to the insensitivity of the flame photometric method for the fluorides. For NaF a chemiluminescent determination [42] led to a lower limit ($D_o^0 \geq 5.33$ eV) in good agreement with the flame photometric result [41], but considerably larger than the generally accepted thermochemical value [1]. The bond energy of CsF is well established experimentally since the bond energies determined by thermochemical [1], photoionization [43], flame photometry [41] and collision-induced dissociation [44] techniques give essential agreement.

Comparing our SCF and CI(SD) D_o values in Table IV, we find that correlation uniformly increases D_o , and that this effect is somewhat larger for the heavier alkali atoms. We have not yet performed the CI(SD) calculation for CsF, but predict a value of about 5.23 eV. This is in excellent agreement with experiment, except for the older thermochemical value of Scheer and Fine [45], which would appear to be about 0.2 eV too low. Overall, our CI(SD) D_o values are in excellent agreement with experiment, especially the thermochemical values of Brewer and Brackett [1].

The CI(SD) D_o values in Table IV should be accurate to about 0.1 eV. Hence, we recommend adopting 5.0 ± 0.1 eV for NaF, which supports the thermochemical

value and is within the error bars of the flame experiments, but which rules out the chemiluminescent value of Ham [42]. We conclude, therefore, that there exists a small (0.3 eV) energy barrier in the formation of the emitting state in his reaction.

The theoretical r_e and ω_e values are compared with experiment in Table V. The agreement with the experimental r_e and ω_e values is excellent. There is a tendency at the SCF level to overestimate the bond length for the heavier alkali atoms where the pair-pair correlation is more important. The fact that the CI(SD) calculations do not fully correct the deficiencies of the SCF may be due to basis set limitations or to the CI(SD) procedure itself, which may underestimate slightly the important differential effect of the pair-pair terms. As one can see from the strong correlation of D_e and r_e in Fig. 1, it is likely that the theoretical D_e values are slightly small for the heavier systems where the CI(SD) r_e values are slightly larger than experiment.

B. Alkaline-earth fluorides

Our theoretical dissociation energies for the alkaline-earth fluorides (Be-Sr) are in excellent agreement with the available experimental values. For BeF we favor the older mass spectrometric determination of Hildenbrand and Murad [46] over the later determination by Farber and Srivastava [47]. Our D_e for BeF includes correlating the Be 1s electrons, which produces a D_e almost 0.1 eV greater than calculations in which the 1s is not correlated. For MgF our D_e of 4.66 eV lies between the two mass spectrometric determinations [48-49]. Since further basis set saturation is likely to increase our value slightly, we favor a value of 4.7 ± 0.1 eV, which is consistent with all available values.

Our CI(SD) D_e for CaF lies within the error bars of the old thermochemical value of Blue et al. [50-51], but clearly suggests that the flame photometry D_e of Ryabova and Gurvich [52] is too large. Apparently, the D_e values for the fluorides determined by flame photometry are systematically large (except for LiF), but are usually correct within the rather large error bounds given. We would recommend adopting our theoretical value or a value slightly larger for CaF. For SrF, our

CI(SD) D_o value agrees with all three experiments within their stated error bounds if one allows a 0.1 eV uncertainty in our value. However, our results again suggest that the flame photometry value [52] is too large and that the Ehlert et al. [48] mass spectrometric determination is too low. We are in excellent agreement with the mass spectrometric determination of Hildenbrand ($D_o = 5.62 \pm 0.07$) [49], and would recommend adopting this value for SrF. Work is presently in progress [23,53] on BaF. Preliminary results are in excellent agreement with experiment [48,49,51].

C. Alkali chlorides

For the alkali chlorides rather reliable experimental values are available for comparison. The flame photometry technique [41] is much more sensitive for the chlorides, and produces values in good agreement with the thermochemical values [1]. Although our CI(SD) D_o values in Table VI are in excellent agreement with experiment, especially for the lighter alkali chlorides (Li-K), there is a tendency for theory to underestimate D_o and overestimate r_e . Whereas the error for RbF is only 0.017\AA , the error for RbCl is 0.043\AA at the CI(SD) level. For the heavier alkali halides where the bonding is predominantly ionic, it is tempting to use the nearly linear relationship between D_o and r_e to "correct" the theoretical D_o values. Allowing for a 0.03 eV change in D_o per 0.01\AA change in r produces "corrected" D_o^{SCF} values of 4.37 eV for KCl and RbCl and 4.54 eV for CsCl in excellent agreement with experiment. One produces similar results for KCl and RbCl by correcting the D_o^{CI} results by 0.02 eV per 0.01\AA change in r , which is approximately the same correction that one would derive from the linear relationship among the alkali chlorides in Fig. 1.

The "corrected" theoretical D_o values provide strong support for the available experimental values. We prefer the thermochemical values of Brewer and Brackett [1] slightly over the flame photometry values of Bulewicz et al. [41], since our theoretical results suggest that the dissociation energy of RbCl is less than or equal to that for KCl. For CsCl we have not yet carried out the CI(SD) calculation, but we estimate a value of 4.4 eV, significantly below the experimental values

[43-44] of 4.58 eV. Whether this is entirely a result of basis set incompleteness or due partially to a tendency of the CI(SD) procedure to underestimate the pair-pair correlation, we hope to elucidate in future work [23].

D. Alkaline-earth chlorides

The agreement between our CI(SD) D_0 values and experiment [54,60] is excellent if we take the lower mass spectrometric determination of 3.98 ± 0.10 eV. [54] for BeCl. The very large positive correlation effect observed for BeCl arises from the large component of covalent character in the bonding. Note that BeCl has a r_x/r_e value of only 1.41 (see Table I). When there is a significant differential correlation effect, there is a tendency to underestimate it, so the mass spectrometric value of Hildenbrand [54] may be correct within their error bars. Thus, we recommend a value of 3.9 ± 0.1 eV for BeCl. For MgCl, we also prefer the lower mass spectrometric determination of 3.26 ± 0.13 . The errors in the bond lengths for the heavier alkaline-earth chlorides are less than the corresponding alkali chlorides (see Table VII). Hence, the CI(SD) D_0 values for CaCl and SrCl are probably only slightly (0.05 eV) too low. Allowing for this the lower bound of 4.29 for SrCl determined from chemiluminescent studies [60] would appear to be slightly high.

E. Alkali oxides

The alkali oxides are unique in that they undergo a change in ground state symmetry from $^2\Pi$ (LiO, NaO) to $^2\Sigma^+$ (KO, RbO, CsO). This has been explained [15] in terms of the competing effects of quadrupole interactions (favoring $^2\Pi$) and Pauli repulsion (favoring $^2\Sigma^+$). Both the theoretical [14-15] and experimental [12-13,64] evidence is that LiO and NaO have $^2\Pi$ ground states, whereas RbO and CsO have $^2\Sigma^+$ ground states. For KO there is conflicting experimental evidence; the ESR spectrum [13] suggests a $^2\Pi$ ground state, whereas a magnetic analysis of the K + NO₂ system [12] suggests a $^2\Sigma^+$ ground state. Previous theoretical results

for KO are conflicting as well, with the SCF calculations of So and Richards [14] giving a $^2\Sigma^+$ ground state, and both the SCF and CI calculations of Allison et. al. [15] giving a $^2\Pi$ ground state.

Our theoretical $^2\Pi - ^2\Sigma^+$ energy separations are compared with previous theoretical and experimental evidence in Table VIII. Throughout we have correlated 15 valence electrons (11 for LiO), which we believe is essential for a balanced treatment of the two states. For all of the alkali oxides we find that the $^2\Pi - ^2\Sigma^+$ energy separation is insensitive to electron correlation, because both states are equally well described by the HF configuration. This is also generally true of previous theoretical results except for the KO results of Allison et al. [15] where they observe a 600 cm^{-1} increase in the separation. However, this increase is probably an artifact of correlating only the oxygen valence electrons without first localizing the orbitals. In KO there is a substantial mixing of the oxygen 2s and potassium 3p orbitals, which is somewhat more pronounced in the $^2\Sigma^+$ state. The greater mixing in the $^2\Sigma^+$ state reduces its correlation energy with respect to the $^2\Pi$ state producing the larger separation. When both the oxygen and metal electrons are correlated with the CI(SD) procedure, the computed energies are invariant to these arbitrary mixings.

Apparently, basis set quality is a more important consideration than electron correlation for an accurate determination of the $^2\Pi - ^2\Sigma^+$ energy separation. This statement is substantiated by the results in Table IX, where we have studied basis set effects on the energy separation in KO at 4.2 Bohr. Starting with the large Slater basis set in Table IX, and selectively deleting functions, we find that deleting the diffuse functions has little effect on the energy, but deleting the 4f functions and particularly the 4f functions on oxygen, has a substantial (250 cm^{-1}) effect on the separation. Apparently, f functions are more important for the $^2\Sigma^+$ state. Similarly, deleting all d- and f-functions results in a very large (960 cm^{-1}) effect on the $^2\Pi - ^2\Sigma^+$ separation, since the d functions are more important for the $^2\Pi$ state. Finally, to assess how close our Slater basis is to the HF limit, we have carried out numerical HF calculations on both the $^2\Pi$ and $^2\Sigma^+$ states. The numerical HF calculations (see Table IX) show that our Slater basis is within 0.018 and 0.015 eV of the HF limit for the $^2\Sigma^+$ and $^2\Pi$ states at 4.20 Bohr, respectively. We obtain a $^2\Pi - ^2\Sigma^+$ separation of -250 cm^{-1} in the HF limit, which lies between our Slater result and that of So and Richards [14]. Hence, we agree with So and

Richards [14], and disagree with Allison et al. [15], who obtain a $^2\Pi$ ground state at the HF level, probably as a consequence of the relatively small basis set employed. Although our results are not definitive, they strongly support the assignment of a $^2\Sigma^+$ ground state for KO. However, the energy separation is probably sufficiently small to allow the population of both states even at room temperature.

The spectroscopic parameters (r_e , ω_e) for the $^2\Pi$ and $^2\Sigma^+$ states of the alkali oxides are summarized in Table X. We observe almost identical bond contractions upon correlation in the $^2\Pi$ states of the alkali oxides as for the $^1\Sigma^+$ states of the alkali fluorides. Hence, a comparison of the CI(SD) and experimental r_e values for the alkali fluorides should provide a good measure of the remaining errors in the corresponding $^2\Pi$ states of the alkali oxides. However, we observe a significantly larger CI(SD) bond contraction in the $^2\Sigma^+$ states, probably because the hole in the $2p_\sigma$ orbital changes the character of the metal-oxygen repulsion. At the CI(SD) level we obtain nearly identical bond lengths for the $^2\Sigma^+$ states of KO and RbO as for the $^1\Sigma^+$ states of KF and RbF. This is significantly different from the assumption of $r_e(\text{MO}) = r_e(\text{MF}) + 0.05\text{\AA}$ made by Herm and Herschbach [12] for purposes of estimating MO dissociation energies based on the corresponding alkali fluorides.

Our theoretical dissociation energies for the alkali oxides (with respect to ground state atoms) are compared with experiment in Table XI. Our results generally agree with the estimates of Herm and Herschbach [12], within their error bounds, illustrating again how well bond energies scale with bond length for these ionic systems. Our CI(SD) dissociation energies for LiO and NaO are significantly larger than the values derived from mass spectrometry [65-66]. In fact, they are larger by about the $^2\Pi - ^2\Sigma^+$ energy separation, which suggests the possibility that these molecules were prepared in the excited $A^2\Sigma^+$ state. Our D_0 for LiO is also significantly larger than the theoretical value of Yoshimine [61], which was obtained by referencing directly to ground state atoms. This procedure underestimates the differential correlation energy thereby underestimating D_0 . We do, however, agree with the theoretical estimate of O'Hare and Wahl [62] of 2.72 ± 0.3 eV for NaO. Apparently, all of the dissociation energies reported by Allison et al. [15] are significantly too low as a result of basis set incompleteness accentuated by their procedure of correlating only eight valence electrons. For KO we are in excellent agreement with the Ehlert [67] mass spectrometric determination, and agree

with the Guseinov and Gorokhov [68] value within their error bounds.

For RbO($^2\Sigma^+$) and CsO($^2\Sigma^+$), there are to our knowledge no experimental values available for comparison, but we are in good agreement with the estimates of Herm and Herschbach [12]. Since our theoretical values tend to be slightly low for the heavier alkali atoms our recommended values are 2.9 ± 0.1 eV for RbO and 3.1 ± 0.1 for CsO. We arrive at the value for CsO by adding to our SCF value a 0.15 eV correction for electron correlation and a 0.05 eV correction for basis set incompleteness.

F. Alkaline-earth oxides

The $^1\Sigma^+$ ground states of the alkaline-earth oxides are not well represented by a single reference configuration reflecting the fact that the charge distribution is intermediate between M^+O^- and $M^{++}O^-$. Therefore, we have applied our method to the $a^3\Pi$ states, ($A^1\Pi$ for BeO) since they are well represented by the SCF reference and the T_e values are known experimentally [69]. For BeO we used the $A^1\Pi$ state since the T_e for the $a^3\Pi$ state is not accurately known. The spectroscopic parameters (r_e , ω_e) are compared with the corresponding experimental values [69] in Table XII. The CI(SD) values are uniformly better than the SCF values, and show errors just slightly larger than for the fluorides.

The CI(SD) D_o values for the alkaline-earth oxides shown in Table XI should be the most consistent set of numbers available, and are thus capable of ruling out incorrect experimental values. Theoretical dissociation energies have been reported for both MgO [8] and CaO [11]. The values reported herein are just slightly larger owing to the larger basis sets employed and the treatment of electron correlation.

Our CI(SD) value of $D_o = 4.69$ eV for BeO is just slightly above the old mass spectrometric value of Chupka et al. [70]. This value includes correlating the Be 1s electrons, and produces a bond length for the $A^1\Pi$ state that is 0.007\AA shorter than experiment. If the Be 1s electrons are not correlated $D_o = 4.60$ eV and $r_e = 1.462\text{\AA}$ in almost perfect agreement with experiment [69]. However, we believe

the higher value of $D_0=4.69$ eV is preferred, and that the experimental values are just slightly too low. Note that we arrive at our values using a $T_e(A^1\Pi^{-1}\Sigma^+)$ of 9405.6 cm^{-1} , and correcting for the zero-point motion in the ground state using $\omega_e=1187.3 \text{ cm}^{-1}$.

All of the available experimental values [2-7] for the $^1\Sigma^+$ state of MgO are substantially too large. The value recommended by Huber and Herzberg [69] is 3.5 eV, which is a reinterpretation of the Srivastava value [7] in Table XI, taking into account the presence of the low-lying $a^3\Pi$ state. In contrast, the theoretical calculations by Bauschlicher et al. obtain $D_0=2.65\pm0.16$ eV. The CI(SD) value reported here of 2.75 ± 0.1 eV is slightly larger as a result of the more extended basis set and CI treatment. Note that this D_0 value is what would be expected based on the nearly linear relationship between bond distance and bond energy shown in Fig. 1. In determining D_0 calculations were performed for the $a^3\Pi$ state, which was presumed to be 0.326 eV above the ground state [71]. Based on a comparison of our computed r_e value for MgF($^1\Sigma^+$) with experiment, our calculations suggest that the somewhat uncertain r_e value of 1.8₇ reported in Huber and Herzberg [69] is slightly long.

For CaO, recent chemiluminescence studies have yielded different values for the dissociation energy. The study of Engelke, Sander and Zare (ESZ) [9] yields a lower bound of $\geq 4.76\pm0.15$ eV, while that of Irvin and Dagdigian (ID) [10] yields 4.11 ± 0.07 eV. The work of ID is in excellent agreement with the older mass spectrometric values [3,7], but the ESZ result was recommended by Huber and Herzberg [69]. Recent SCF calculations by Bauschlicher and Partridge [11] gave strong support for the determination of ID. Our CI(SD) result of 4.14 ± 0.1 is also in excellent agreement with the chemiluminescent value of ID. We thus recommend adopting this value for CaO, which again places the value on the linear plot of Fig. 1. The higher value is now thought to be in error as a result of interference with CaCl.

For the SrO molecule there is again an apparent discrepancy between the recent chemiluminescence studies of ESZ [9] that gave a lower bound of $D_0\geq 4.67\pm0.15$ eV, and the older mass spectrometry and flame photometry values. Our value is in excellent agreement with the value recommended by Srivastava [7] in a review of the experimental literature prior to 1975. We expect our value is

slightly (≈ 0.05 eV) too low judging from an overestimation of the bond length by 0.02\AA . Hence, we would recommend a value of 4.36 ± 0.10 eV that rules out the determination by ESZ. The ESZ lower bound for SrO was based on the identification of a small spectral feature as the (18,0) band of the SrO $A^1\Pi-X^1\Sigma^+$ system (see Fig 3 of [9]). However, owing to the strong interference from SrCl, all that can be safely determined is that the (11,0) band is populated. Since the (18,0) band is at $17,420\text{ cm}^{-1}$ and the (11,0) band is at $14,237\text{ cm}^{-1}$, 3203 cm^{-1} should be removed from the lower bound, giving a revised estimate [72] of $D_o(\text{SrO}) \geq 4.27 \pm 0.15$ eV.

For BaO we have not yet carried out the CI(SD) treatment, but have determined an SCF value of 5.61 eV. Since we anticipate that D_o will increase by at least 0.1 eV with the CI(SD) treatment as well as with further basis set saturation, we recommend a value of 5.75 ± 0.10 eV. Although the error bars given for BaO may be somewhat optimistic, our recommended value is in good agreement with the lower bound of $\geq 5.79 \pm 0.15$ eV given by ESZ [9] determined from the chemiluminescence spectrum of Ba + ClO₂. Note also that their determination for BaO seems much more definitive since there is no interference from BaCl (see Fig. 2 of [9]).

G. Alkali sulfides

We are unaware of any experimental work on the alkali sulfides (MS) which are difficult to observe as a result of their strong tendency to form M₂S. In Table XIII we have summarized our theoretical MS($X^2\Pi$) D_o values and $X^2\Pi-A^2\Sigma^+$ energy separations for the alkali sulfides LiS-RbS. The ground states for all of these systems are definitively determined to be $X^2\Pi$. Although calculations have not yet been done for CsS, we predict a $^2\Pi$ ground state as well. The $^2\Pi$ states would appear to be more stable with respect to the $^2\Sigma^+$ states in the sulfides than the oxides, because the considerably longer bond lengths ($r_e(\text{MS}) \approx 1.22r_e(\text{MO})$, M=Na, K, Rb) reduce the importance of the Pauli repulsion terms.

The spectroscopic parameters (r_e , ω_e) for the $X^2\Pi$ and $A^2\Sigma^+$ states of the alkali

sulfides (Li-Rb) are given in Table XIV. For the $X^2\Pi$ state we observe a nearly identical bond contraction upon correlation as observed for the $^1\Sigma^+$ states of the corresponding alkali chlorides. For the $A^2\Sigma^+$ states we observe a larger CI bond contraction than in the $^2\Pi$ states, in analogy with the alkali oxides.

Since the $X^2\Pi$ states of the alkali sulfides have considerable analogy with the $X^1\Sigma^+$ states of the corresponding alkali chlorides, we expect the same deficiencies in the CI(SD) D_0 values and bond lengths of the heavier alkali sulfides (KS, RbS) as for the chlorides. Thus, in determining our recommended D_0 values in Table XIX, we have added 0.06 and 0.08 eV, respectively, based on the known deficiencies in our D_0 values of the corresponding alkali chlorides. Note that the alkali sulfides obey the nearly linear relationship between dissociation energy and bond length illustrated in Fig 1, even though by the r_x/r_e criterion they are far less ionic than the corresponding chlorides.

H. Alkaline-earth sulfides

For the alkaline-earth sulfides (BeS-CaS) we have encountered the same problem as for the oxides, namely that the $X^1\Sigma^+$ ground states are not well described by a single reference configuration, and therefore not amenable to our model. Therefore, we have considered instead the $A^1\Pi$ and $a^3\Pi$ states, which are both equally well described by a single reference configuration. Our theoretical spectroscopic parameters (r_e , ω_e , D_e) for the $A^1\Pi$ states of BeS, MgS and CaS as well as the $a^3\Pi-A^1\Pi$ energy separations are summarized in Table XV. The corresponding spectroscopic parameters (r_e , ω_e) for the $a^3\Pi$ state (not reported) are essentially identical to those for the $A^1\Pi$ state. The theoretical $a^3\Pi-A^1\Pi$ energy separations for the sulfides decrease down the column as the $K(\sigma,\pi)$ exchange integral decreases with increasing internuclear distance since the σ open-shell orbital is localized on the metal, and the π electron is primarily a $3p\pi$ sulfur orbital. The singlet-triplet separations are comparable or slightly smaller for BeS and MgS than for the corresponding oxides [73-76].

To convert our dissociation energies for the $A^1\Pi$ states in Table XV to ground

state D_o , we must add $T_e(A^1\Pi)$ and subtract the $X^1\Sigma^+$ zero-point energy. Unfortunately, $T_e(A^1\Pi)$ is known only for BeS, and even here the vibrational numbering in the $A^1\Pi$ state is uncertain by one unit [77]. Using $T_e(A^1\Pi)=7842.9 \text{ cm}^{-1}$ and $\omega_e(X^1\Sigma^+)=997.94$, our $D_o(X^1\Sigma^+)$ for BeS is 3.20 eV. The theoretical value is consistent with the rather uncertain value of 3.47 ± 0.65 eV reported in the JANAF tables [78]. A linear Birge-Sponer extrapolation of the ground state with corrections for ionic character [79] and excited state products yields a value of 3.30 eV [78].

Our theoretical dissociation energy (D_e) for the $A^1\Pi$ state of MgS is 1.70 eV. If we assume in analogy with MgO that the $A^1\Pi$ state is low-lying (assuming $T_e=3000 \text{ cm}^{-1}$ following JANAF, we obtain $D_o(X^1\Sigma^+)=2.04$ eV, which is considerably lower than the rather uncertain JANAF value [78] of 2.86 ± 0.69 eV. Hence, it is likely that like MgO, the JANAF value for MgS is significantly too large.

Our CI(SD) dissociation energy for the $A^1\Pi$ state of CaS is 2.41 eV. Adopting the rather uncertain JANAF estimate of 7200 cm^{-1} for $T_e(A^1\Pi)$, produces a $D_o(X^1\Sigma^+)$ of 3.27 eV in excellent agreement with the mass spectrometric studies of Colin et al. ($D_o=3.20 \pm 0.20$ eV) [80], but less than that of Marquart and Berkowitz (3.45) [81]. This suggests that the $a^3\Pi$ and $A^1\Pi$ excitation energies for the alkaline-earth sulfides are reasonably similar to the corresponding oxides. Theoretical work is in progress to accurately determine these excitation energies [26].

I. Alkali hydroxides

Our theoretical dissociation energies for the alkali and alkaline-earth hydroxides are compared to experiment [82-97] in Table XVI. The most striking feature of the alkali hydroxides (especially the heavier ones) is their similarity to the alkali fluorides. The dissociation energies of the hydroxides are less than the fluorides by slightly less than the electron affinity difference ($EA(F)-EA(OH)=1.57$ eV) [21,98].

Comparison of the alkali hydroxides with the alkali oxides is also enlightening. Here the electron affinity difference ($EA(OH)-EA(O) \approx 0.37$) is only about half of

the difference in dissociation energies ($D_o(MOH) - D_o(MO)$). The increased stability of the hydroxides relative to the oxides is a result of the ability of the hydrogen atom to pull charge density out of the metal oxygen bond, thereby reducing the bond length and giving rise to greater electrostatic interaction [99]. The increased stability of the alkali hydroxides with respect to the oxides is also evident from the plot of D_e versus r_e in Fig. 1.

The theoretical CI(SD) D_o values for the alkali hydroxides are in reasonably good agreement with the two sets of experimental values derived from atomic absorption spectroscopy in flames. The theoretical values are probably more accurate than the flame values, in part because the experimental values are based on equilibrium constants, which in turn require a knowledge of the rotational and vibrational partition functions of MOH. Our theoretical values for the hydroxides should be almost as accurate as for the fluorides, and show an amazing parallel. There is a tendency for theory to overestimate the bond length slightly for the heavier alkali hydroxides. Hence, based on the nearly linear relationship between bond length and D_e , our recommended values in Table XIX add 0.02, 0.04 and 0.06 to our CI(SD) D_o for KOH, RbOH and CsOH, respectively. These changes improve agreement with experiment, but our recommended value for CsOH of 3.77 ± 0.10 eV is still considerably less than the experimental values [82,84]. Note that the difference in dissociation energy of CsOH and RbOH obtained from the two flame experiments was quite different (0.13 eV versus 0.34 eV). We obtain about 0.19 eV for this difference, which is essentially the same as the difference in dissociation energy of CsF and RbF.

Our theoretical r_e and ω_e values for the alkali hydroxides are compared with experiment [100-109] in Table XVII. These results were obtained assuming a fixed OH bond length of 0.947\AA . If we correct our CI(SD) r_e values for the hydroxides by the known deficiencies in the CI(SD) values of the corresponding fluorides, then we are in satisfactory agreement with the rather uncertain experimental values, except for NaOH. For NaOH we estimate a Na-O bond length of 1.936\AA , which is significantly shorter than the experimental estimate [101] of 1.95\AA . Our theoretical ω_e values for the alkali hydroxides tend to be slightly larger than the corresponding fluorides, arising primarily from the difference in mass, i.e. $(M_O + M_H) < M_F$. The theoretical ω_e values are probably the most accurate available. For CsOH we agree with the rather uncertain gas phase value [106]. However, our

results imply that all of the ω_e values derived from matrix isolation studies [102,104,107] are systematically low.

J. Alkaline-earth hydroxides

The similarity of the alkaline-earth hydroxides and fluorides is demonstrated by the recent high-resolution laser excitation spectra of CaOH [108] and SrOH [109]. The lowest electronic transitions for both the alkali fluorides and hydroxides involves the promotion of a nonbonding electron localized primarily in the metal $n\sigma$ orbital to a metal $np\pi$ or $np\sigma$ orbital. Since these transitions are localized primarily on the metal, the potential curves for each state are similar, giving a spectrum consisting of very strong, badly overlapped $\Delta v=0$ sequences.

The theoretical dissociation energies of the alkaline-earth hydroxides are smaller than the corresponding fluorides by less than the difference of 1.57 in the electron affinities of F and OH. Again this demonstrates the increased stability of the hydroxides that arises from the ability of hydrogen to pull charge out of the metal-oxygen bond. Experimental studies of the alkaline-earth hydroxides in flames are complicated by the presence of the dihydroxide. In general, the flame-spectral data appear to give dissociation energies that are too high. The experimental values for BeOH are particularly uncertain. Our D_0 value of 4.70 eV for BeOH is within the error bounds of the value of 4.94 ± 0.43 reported in the JANAF Tables [87], which is the average of two values ascribed to Inami and Ju [86]. The considerably larger D_0 value of Ko et al. [85] for BeOH was discarded based on a comparison of the trends in the alkaline-earth hydroxides and halides. Note that our value of $D_0 = 4.70$ eV was determined for a linear geometry and includes correlating the Be 1s electrons. However, calculations with a smaller gaussian basis set lead to a bent ($\theta = 33^\circ$) equilibrium structure about 0.01 eV more stable than the linear one.

For MgOH, the two older experimental values of $D_0 = 2.43 \pm 0.22$ eV derived by Bulewicz and Sugden [89] from flame spectra studies, and $D_0 = 4.16 \pm 0.13$ eV derived by Cotton and Jenkins [88] using atomic absorption spectroscopy appear

to be in error. The JANAF Tables [87] have adopted an intermediate value of 3.59 ± 0.22 eV, which is based primarily on the trends between the hydroxides and halides. There is also a more recent mass spectrometric determination [90] of 3.19 ± 0.22 eV that is more reliable. Our theoretical value of $D_0 = 3.31$ eV is somewhat larger, but agrees with the mass spectrometric determination within its error bars.

For the heavier alkaline-earth hydroxides, there is a larger body of reliable experimental D_0 values. Our theoretical D_0 for BaOH appear to be systematically low by ≈ 0.2 eV as a result of using a relativistic effective core potential. Hence for BaOH we are only able to recommend a value of $D_0 = 4.6 \pm 0.2$ eV, which includes all of the experimental values [90,93,97] except that of Cotton and Jenkins [92], which appears to be too high as are their values for CaOH and SrOH.

For CaOH and SrOH our CI(SD) D_0 values agree with the mass spectrometric determinations [90] within their error bounds, but strongly suggest that the values are systematically 0.10-0.15 eV low for the hydroxides of Mg, Ca and Sr. The lower flame values of Gurvich et al. [96] for SrOH and Ryabova et al. [93] for CaOH agree quite well with our theoretical values. Overall, our theoretical values should be the most reliable, and may be capable of shedding light on the relative equilibrium constants for the formation of the mono- and di-hydroxides.

The theoretical spectroscopic constants r_e and ω_e for the alkaline-earth hydroxides are summarized in Table XVII. These were determined using a fixed OH bond length of 0.947\AA . For BeOH we obtain a non-linear equilibrium structure with an equilibrium bond angle of about 33° . The heavier alkaline-earths all favor linear structures, but are exceptionally flat in the bending potential. The ω_e values for the alkaline-earth hydroxies are about 10% greater than the corresponding fluorides. Our ω_e values for CaOH and SrOH are in very good agreement with the gas phase values [108,109]. Little is known about the equilibrium bond lengths for the alkaline-earth hydroxides. Our CI(SD) values for CaOH and SrOH are slightly larger than the gas phase values [108,109] as expected. However, our r_e values for BeOH and MgOH should be quite accurate (see corresponding fluorides).

K. Alkaline-earth isocyanides

We summarize here the theoretical calculations [110] that were undertaken to determine the lowest energy structures and dissociation energies for the $^2A'$ ground-state surfaces of MCN (M=Be, Mg, Ca and Ba). There has been considerable interest in the corresponding alkali cyanide molecules recently with the discovery that both NaCN and KCN have non-linear T-shape equilibrium structures [111-115]. The dominant features in the spectra of the alkaline-earth (iso)cyanides are broad "quasicontinua", that occur at nearly the same wavelengths as the spectra of the homologous alkaline-earth monohalides [116]. These molecules are also expected to be ionic based on the successive change in electronegativities $\text{Cl} < \text{CN} < \text{F}$. Note, however, that the electron affinity [117] of CN, 3.82 ± 0.02 , is considerably greater than even that of fluorine (3.399 eV).

For all of the alkaline-earths studied, the linear isocyanide structure was found to be the most stable. At the CI(SD) level, the cyanide structure was found to lie above the isocyanide structure by 0.26 eV for Be, 0.13 eV for Mg and 0.20 eV for Ca. One interesting change in going from BeCN to BaCN is the loss of the interconversion barrier between the isocyanide and cyanide structures. On the basis of several cuts through the potential surface, we found an interconversion barrier for BeCN and MgCN, but none for the heavier alkaline-earths, where the bonding becomes increasingly ionic.

Our theoretical dissociation energies for the cyanide, isocyanide and bond-mid-point (metal atom approaching CN bond midpoint) structures are compared with experiment in Table XVIII. The experimental dissociation energies [118] for the monocyanides have been determined using electrothermal atomic absorption spectrometry. These values contain considerable uncertainty, since little was known about the number of low-lying electronic states, geometry or force constants of these molecules. The experimental values lie consistently above our values, particularly for MgCN which we feel must contain some systematic error. On the other hand, our value for the BaCN structures are probably 0.2 eV too low as a result of using a relativistic effective core potential treatment of the core.

Our dissociation energies for the isocyanides are very similar to the

corresponding chlorides. This correlation provides additional support for our theoretical value for MgCN. Apparently, the delocalization of charge in CN makes the D_e of the isocyanides more comparable to the chlorides, even though the M-NC bond lengths are intermediate between the corresponding alkaline-earth fluorides and chlorides.

I. Conclusions

The theoretical dissociation energies presented here for most of the alkali and alkaline-earth fluorides, chlorides, oxides, sulfides, hydroxides and isocyanides are sufficiently accurate to rule out disparate experimental values. Overall, we find that the thermochemical and mass spectrometric determinations of D_0 are quite accurate. The D_0 values determined by flame photometry are often accurate, but tend to be systematically high (especially for the fluorides). Finally, we find that D_0 values determined from chemiluminescent studies, although potentially very accurate, are often incorrect.

An advantage of treating several classes of systems in a systematic way, is that trends in the dissociation energies emerge more clearly. For example, the MF and MOH bond lengths are comparable, and the difference in dissociation energies is slightly less than the electron affinity difference of 1.57 eV. However, the isocyanides have distinctly smaller dissociation energies than the fluorides even though the electron affinity of CN is substantially greater than that of F. The difference arises because the charge is spread out in CN, but localized on oxygen in OH.

The theoretical D_0 values in conjunction with the available experimental values allow us to recommend reliable D_0 values for all systems considered. These recommended values in Table XIX are thought to be accurate to 0.1 eV. The model we have applied seems to be satisfactory even for systems (e.g. BeCl) that are not fully ionic as long as we account for differential correlation effects with the CI(SD) procedure. We are willing to calculate the dissociation energy of any other diatomic or triatomic system that fits our model, if it is of sufficient scientific interest.

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Table I. Ratio r_x/r_e for selected alkali and alkaline earths

Molecule	$r_e(\text{\AA})^a$	$r_x(\text{\AA})^b$	Ratio
LiF(${}^1\Sigma^+$)	1.564	7.232	4.62
LiCl(${}^1\Sigma^+$)	2.021	8.113	4.01
LiO(${}^2\Pi$)	1.695	3.666	2.16
LiS(${}^2\Pi$)	(2.163)	4.347	2.01
NaF(${}^1\Sigma^+$)	1.926	8.280	4.30
NaCl(${}^1\Sigma^+$)	2.361	9.455	4.01
NaO(${}^2\Pi$)	(2.040)	3.917	1.92
NaS(${}^2\Pi$)	(2.487)	4.705	1.89
KF(${}^1\Sigma^+$)	2.171	15.319	7.06
KCl(${}^1\Sigma^+$)	2.667	19.889	7.46
KO(${}^2\Sigma^+$)	(2.187)	5.005	2.29
KS(${}^2\Pi$)	(2.843)	6.367	2.24
RbF(${}^1\Sigma^+$)	2.270	18.533	8.16
RbCl(${}^1\Sigma^+$)	2.787	25.668	9.21
RbO(${}^2\Sigma^+$)	(2.288)	5.306	2.32
RbS(${}^2\Pi$)	(2.983)	6.861	2.30
BeF(${}^2\Sigma^+$)	1.361	2.432	1.79
BeCl(${}^2\Sigma^+$)	1.797	2.524	1.41
BeO(${}^1\Sigma^+$)	1.331	1.832	1.38
BeS(${}^1\Sigma^+$)	1.742	1.988	1.14
MgF(${}^2\Sigma^+$)	1.750	3.392	1.94
MgCl(${}^2\Sigma^+$)	2.199	3.574	1.63
MgO(${}^1\Sigma^+$)	1.749	2.329	1.33
MgS(${}^1\Sigma^+$)	2.143	2.587	1.21
CaF(${}^2\Sigma^+$)	1.967	5.310	2.70
CaCl(${}^2\Sigma^+$)	2.439	5.769	2.37
CaO(${}^1\Sigma^+$)	1.822	3.097	1.70
CaS(${}^1\Sigma^+$)	2.318	3.570	1.54
SrF(${}^2\Sigma^+$)	2.075	6.280	3.03
SrCl(${}^2\Sigma^+$)	2.576	6.933	2.69
SrO(${}^1\Sigma^+$)	1.920	3.404	1.77
SrS(${}^1\Sigma^+$)	2.441	3.984	1.63

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^aBond distances in parentheses are theoretical values for cases where experimental values are unavailable.

^bHypothetical crossing point where a purely ionic potential curve ($1/R$) crosses the ground state asymptote.

Table II. Summary of Slater and gaussian basis sets

A. Slater Basis sets

Atom	Basis size	Basis set description ^a
O	7s5p3d1f	Clementi ^b (6s4p) O and O ⁻ basis. Polarization functions optimized for O and O ⁻ ^c
F	6s5p4d2f	Clementi (6s4p) F and F ⁻ basis. Polarization functions optimized for F and F ⁻ ^d
S	9s7p3d2f	Clementi (7s6p) S ⁻ basis. Even tempered d and f functions optimized at the CI(SD) level.
Cl	9s7p3d2f	Clementi (7s6p) Cl ⁻ basis. Even tempered d and f functions optimized at the CI(SD) level.
Li	6s6p4d2f	Konowalow ^e (5s5p3d) basis
Li(1s)	6s8p6d2f	Adds compact 2p (4.0, 8.0) and 3d (5.0, 8.0)
Na	8s6p4d2f	Clementi (7s,3p) basis
K	10s8p4d2f	Clementi (11s6p) basis with two most diffuse s functions deleted
Rb	11s9p6d2f	Clementi (11s7p3d) Rb basis minus most diffuse s
Cs	14s11p9d2f	McLean ^f (10s8p4d) Cs ⁺ basis reoptimized
Be	6s4p3d1f	Liu ^g Be ₂ basis
Be(1s)	6s6p5d2f	Adds 2p(6.0, 3.5), 3d(8.0, 4.0) and 4f(2.8)
Mg	8s6p4d2f	8s6p4d1f basis used for MgO ^h
Ca(3d)	10s8p3d2f	Ca basis used for CaO ⁱ 3d(0.8007, 2.122, 4.77)
Ca(4d)	10s8p4d2f	Even tempered d basis 3d(0.75, 1.5, 3.0, 6.0)

Sr	$13s10p7d3f$	Clementi (11s7p3d) Sr^+ basis reoptimized. Valence exponents optimized for the $Sr\ ^3P$ and 3D states.
Ba	$15s13p9d3f$	McLean (12s8p4d) Ba^+ basis reoptimized. Valence exponents optimized for the $Ba\ ^3P$ and 3D states.

B. Gaussian basis sets

O	(11s7p3d1f/6s4p3d1f)	van Duijneveldt ^j 11s6p.
H	(8s4p/5s3p)	van Duijneveldt 6s.
C	(11s7p2d/6s4p2d)	van Duijneveldt 11s6p.
	(11s7p3d1f/6s4p3d1f)	Expanded d and f basis.
N	(11s7p2d/6s4p2d)	van Duijneveldt 11s6p.
	(11s7p3d1f/6s4p3d1f)	Expanded d and f basis.
Li	(11s7p7d4f/7s7p7d3f)	van Duijneveldt 11s.
Be	(11s5p2d/7s3p2d)	van Duijneveldt 11s.
	(11s6p7d4f/7s6p7d3f)	Tight p and expanded d and f basis.
Na	(12s9p6d3f/7s6p5d2f)	McLean and Chandler ^k 12s9p.
Mg	(12s9p5d/6s6p4d)	McLean and Chandler 12s9p.
	(12s9p6d4f/6s6p5d3f)	Expanded d and f basis.
K	(15s13p6d4f/9s9p5d3f)	Wachters ^l 14s9p.
Ca	(15s13p5d/9s9p3d)	Wachters 14s9p.
	(15s13p7d2f/9s9p6d2f)	Expanded d and f basis.
Rb	(18s14p11d4f/12s10p5d3f)	Huzinaga ^m 17s11p6d.
Sr	(17s14p11d4f/11s9p5d2f)	Huzinaga 17s11p6d.
Cs	(14s9p6d4f/7s7p5d3f)	RECP of Christiansen and Laskowski ⁿ , modified valence basis.
Ba	(8s9p6d/6s7p4d)	RECP of Mascarello and Jaffe ^o .
	(8s9p6d4f/7s7p4d3f)	Recontracted s basis and added f functions.

^aA full description of the basis sets is given in the complete works, [23-28].

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Table III. Correlation effects on D_e and r_e in the $X^2\Sigma^+$ ground state of NaF

Description	D_e (eV)	r_e (Å)
HF	4.957	1.924
CI(SD) 8 electrons on F ^a	4.876 ^b	1.944
CI(SD) 8 electrons on Na ^a	4.956	1.934
CI(SD) 8 electrons on F +pair-pair terms ^a	5.034	1.912
CI(SD) 16 electrons	5.023	1.922

^a Orbitals were first localized using corresponding orbitals [30] by maximizing the overlap with the Na^+ orbitals.

^b D_e is 4.83 eV if the orbitals are not localized.

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Table IV. Dissociation energies (D_o) of the alkali and alkaline-earth fluorides

Molecule	Theoretical D_o (eV) ^a	Experimental D_o (eV)
LiF	6.05(6.06)	5.90 ± 0.35^b , 5.96 ^c
NaF	4.92(4.99)	5.25 ± 0.30^b , 4.94 ^c , $\geq 5.33 \pm 0.13^d$
KF	4.96(5.07)	5.07 ± 0.35^b , 5.10 ^c
RbF	4.90(5.04)	5.20 ± 0.35^b , 5.04 ^c
CsF	5.06(-----)	5.33 ± 0.35^b , 5.19 ^c , 5.27 ± 0.06^e , 5.32 ± 0.08^f
BeF	5.88(5.94)	5.85 ± 0.10^g , 6.25 ^h
MgF	4.64(4.66)	4.79 ± 0.05^i , 4.62 $\pm 0.10^j$
CaF	5.43(5.51)	5.4 ± 0.2^k , 5.85 $\pm 0.30^l$
SrF	5.47(5.58)	5.62 ± 0.07^i , 5.43 $\pm 0.10^j$, 5.72 $\pm 0.30^l$

^aSCF results given first with CI(SD) results in parentheses. Zero-point correction is one-half corresponding ω_e .

^bBulewicz, Phillips and Sugden(1961) [41], flame photometry.

^cBrewer and Brackett(1961) [1], thermochemical(298K).

^dHam(1974) [42], chemiluminescent studies.

^eBerkowitz(1971) [43], photoionization.

^fParks and Wexler(1984) [44], collision induced dissociation.

^gHildenbrand and Murad(1966) [46], mass spectrometry.

^hFarber and Srivastava(1974) [47], mass spectrometry.

ⁱHildenbrand(1968) [49], mass spectrometry at 298K.

^jEhlert, Blue, Green and Margrave(1964) [48], mass spectrometry at 298K.

^kBlue, Green, Bautista and Margrave(1963) [50], thermochemical at 298K.

^lRyabova and Gurvich(1964) [52], equilibria in flames.

Table V. Theoretical spectroscopic parameters (r_e , ω_e) for the ground states of the alkali and alkaline-earth fluorides

Molecule ^a	$r_e(\text{\AA})^b$			$\omega_e(\text{cm}^{-1})^b$		
	SCF	CI(SD)	Expt ^c	SCF	CI(SD)	Expt ^c
LiF	1.554	1.557	1.564	926	937	910
NaF	1.924	1.922	1.926	534	531	536
KF	2.205	2.185	2.171	402	437	428
RbF	2.311	2.287	2.270	367	377	376
CsF	2.400		2.345	327	352	
BeF	1.353	1.358	1.361	1220	1224	1247.36
MgF	1.740	1.746	1.750	731	729	711.69
CaF	1.980	1.966	1.967	611	595	581.1
SrF	2.104	2.086	2.075	478	524	502.4

^aThe ground state is ${}^1\Sigma^+$ for the alkali fluorides and ${}^2\Sigma^+$ for the alkaline-earth fluorides.

^bSpectroscopic parameters are based on a parabolic fit to the lowest energy points on a 0.1 Bohr grid.

^cValues taken from Huber and Herzberg [69].

Table VI. Dissociation energies (D_o) of the alkali and
alkaline-earth chlorides

Molecule	Theoretical D_o (eV) ^a	Experimental D_o (eV)
LiCl	4.79(4.89)	4.79 ± 0.13^b , 4.85 ^c
NaCl	4.08(4.21)	4.23 ± 0.09^b , 4.23 ^c
KCl	4.15(4.31)	4.32 ± 0.09^b , 4.39 ^c
RbCl	4.10(4.28)	4.40 ± 0.09^b , 4.37 ^c
CsCl	4.19(-----)	4.65 ± 0.13^b , 4.61 ^c , 4.58 ± 0.07^d 4.58 ± 0.08^e
BeCl	3.57(3.87)	3.98 ± 0.10^f , 4.51 ^g
MgCl	3.08(3.24)	3.26 ± 0.13^h , 3.36 ± 0.02^i
CaCl	3.92(4.10)	4.09 ± 0.13^h , 4.15 ± 0.13^j , 4.08 ± 0.07^k
SrCl	4.04(4.17)	4.16 ± 0.13^h , 4.15 ± 0.08^k , $\geq 4.29^l$

^aSCF results given first with CI(SD) results in parentheses.

^bBulewicz, Phillips and Sugden(1961) [41], flame photometry.

^cBrewer and Brackett(1961) [1], thermochemical(298K).

^dBerkowitz(1969) [43], photoionization mass spectrometry.

^eParks and Wexler(1984) [44], collision-induced dissociation.

^fHildenbrand and Theard(1969) [54], mass spectrometry.

^gFarber and Srivastava(1973) [55], mass spectrometry.

^hHildenbrand(1970) [56], mass spectrometry.

ⁱFarber and Srivastava(1976) [57], mass spectrometry.

^jZmbov(1969) [58], mass spectrometry.

^kGurvich,Ryabova and Khitrov(1974) [59], flame photometry.

^lJonah and Zare(1971) [60], chemiluminescent.

Table VII. Theoretical spectroscopic parameters (r_e , ω_e) for the ground states of the alkali and alkaline-earth chlorides

Molecule ^a	$r_e(\text{\AA})^b$			$\omega_e(\text{cm}^{-1})^b$		
	SCF	CI(SD)	Expt	SCF	CI(SD)	Expt ^c
LiCl	2.036	2.018	2.021	675	668	643
NaCl	2.390	2.366	2.361	362	354	366
KCl	2.740	2.698	2.667	258	273	281
RbCl	2.877	2.830	2.787	223	235	228
CsCl	3.024	-----	2.906	196	-----	214.17
BeCl	1.812	1.797	1.797	865	853	846.7
MgCl	2.212	2.199	2.199	478	469	462.12
CaCl	2.502	2.458	2.439	355	322	367.53
SrCl	2.645	2.607	2.576	287	304	302

^aThe ground state is ${}^1\Sigma^+$ for the alkali chlorides and ${}^2\Sigma^+$ for the alkaline-earth chlorides.

^bSpectroscopic parameters are based on a parabolic fit to the lowest energy points on a 0.1 Bohr grid.

^cValues taken from Huber and Herzberg [69]. For SrCl we used the value ascribed to T. Torring in Table A7.2 of the Ph. D thesis of P. Bernath(MIT).

Table VIII. $^2\Pi - ^2\Sigma^+$ excitation energies of the alkali oxides

Molecule	$^2\Pi - ^2\Sigma^+$ excitation energies (cm^{-1})		
	This work ^a	Other Theory	Expt
LiO	2359(2391)	2894(2634) ^b , 2342(2330) ^c	>0 ^g
NaO	1429(1701)	2088(2177) ^b , 1236 ^d , 1785 ^e	>0 ^h
KO	-205(-240)	233(831) ^b , -347 ^d	? ⁱ
RbO	-516(-650)	-138(-114) ^b , -606 ^d	<0 ^j
CsO	-798(-----)	-735(-846) ^b , -497(-726) ^f	<0 ^{h,j}

^a HF results given first with the CI results in parentheses.

^b (SCF/8-electron CI) results of Allison et al. [15].

^c (SCF/CI) results of Yoshimine [61].

^d SCF results of So and Richards [14].

^e SCF results of O'Hare and Wahl [62].

^f (SCF/CI) results of Laskowski et al. [63].

^g Freund et al. [64].

^h Herm and Herschbach [12].

ⁱ Evidence has been presented separately for both a $^2\Sigma^+$ [12], and a $^2\Pi$ [13] ground state.

^j Lindsay et al. [13].

Table IX. Basis set study of KO at the HF level^a

Basis set Description	<u>Energy(eV)^b</u>	
	$^2\Pi$	$^2\Sigma^+$
NHF	-.015	-.018
[18s14p8d4f] ^b	0.0	0.0
-diffuse functions(df)	0.0035	0.0030
-df and O(4f)	0.0042	0.029
-all f-functions	0.020	0.052
-all f-functions	0.359	0.320
and all d-functions on K		
-all d- and f-functions	0.608	0.489

^a All calculations done at 4.20 Bohr.

^b All energies are given relative to the [18s14p8d4f] Slater calculation. The basis set consists of the potassium and oxygen basis sets in Table II plus a set of diffuse s, p, d and f functions on oxygen. The numerical Hartree Fock (NHF) energies at 4.2 Bohr are -674.01582 a.u. for the $^2\Sigma^+$ state and -674.01249 a.u. for the $^2\Pi$ state.

Table X. Theoretical spectroscopic parameters (r_e , ω_e) for the $^2\Pi$ and $^2\Sigma^+$ states of the alkali oxides^a

Molecule	$r_e(\text{\AA})^b$		$\omega_e(\text{cm}^{-1})^b$	
	$^2\Pi$	$^2\Sigma^+$	$^2\Pi$	$^2\Sigma^+$
LiO	1.674(1.677)	1.579(1.574)	816(805)	767(757)
NaO	2.046(2.040)	1.953(1.943)	519(511)	553(543)
KO	2.351(2.329)	2.225(2.187)	409(396)	417(439)
RbO	2.466(2.443)	2.334(2.288)	328(349)	366(380)
CsO	2.562(-----)	2.426(-----)	327(-----)	331(-----)

^aSpectroscopic parameters are based on a parabolic fit to the lowest energy points on a 0.1 Bohr grid.

^bThe SCF values are given first with the CI(SD) values given in parentheses.

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Table XI. Dissociation energies (D_o) of the alkali and alkaline-earth oxides

Molecule	Theoretical D_o (eV) ^{a-c}	Experimental D_o (eV)
LiO($^2\Pi$)	3.79(3.78)	3.56 ± 0.17^d , 3.49 ± 0.06^e
NaO($^2\Pi$)	2.75(2.83)	2.90 ± 0.13^d , 2.61 ± 0.20^f
KO($^2\Sigma^+$)	2.76(2.86)	3.08 ± 0.13^d , 2.86 ± 0.13^g , 3.08 ± 0.26^h
RbO($^2\Sigma^+$)	2.74(2.88)	2.95 ± 0.13^d
CsO($^2\Sigma^+$)	2.90(-----)	3.03 ± 0.13^d
BeO	4.61(4.69)	4.6 ± 0.1^i , 4.53 ± 0.13^j
MgO	2.71(2.75)	3.71 ± 0.13^j , 3.73 ± 0.22^k
CaO	4.07(4.14)	3.95 ± 0.09^j , $>4.76 \pm 0.15^l$, 4.11 ± 0.07^m 4.03 ± 0.22^k
SrO	4.23(4.32)	4.27 ± 0.09^j , $>4.27 \pm 0.15^{l,n}$
BaO	5.61(-----)	5.62 ± 0.04^j , $\geq 5.79 \pm 0.15^l$

^aSCF values are given first with CI(SD) values given in parentheses.

^bFor the alkali oxides we report D_o values for the designated ground state with respect to ground state atoms even though the $^2\Sigma^+$ states dissociate to M(2P) + O(3P). Zero-point corrections are made using the calculated ω_e values.

^cFor the alkaline-earth oxides, D_o values are reported for the $X^1\Sigma^+$ state with respect to ground state atoms. Zero-point corrections are made using the experimental ω_e values.

^dEstimate of Herm and Herschbach, [12] based on the alkali halide molecules.

^eHildenbrand(1972) [65], electron-impact mass spectrometry.

^fHildenbrand and Murad(1970) [66], mass spectrometry.

^gEhlert(1977) [67], mass spectrometry at 298K.

^hGusarov and Gorokhov(1971) [68], third-law treatment of mass-spectrometric effusion data.

ⁱChupka, Berkowitz and Giese(1959) [70], mass spectrometry.

^jSrivastava(1976) [7], recommended values- review of experimental literature through 1975. See also papers by Farber and Srivastava [6,47,55,57].

^kDrowart, Exsteen and Verhaegen (1964) [3], mass spectrometry.

^lEngelke, Sander and Zare(1976) [9], chemiluminescent studies.

^mIrvin and Dagdiagian(1980) [10], chemiluminescent studies.

ⁿThe value given is the reinterpreted one (see text). Original value was
 $D_o \geq 4.67 \pm 0.15$ eV.

Table XII. Theoretical spectroscopic parameters (r_e , ω_e) for the $A^1\Pi$ state of BeO and the $a^3\Pi$ states of MgO, CaO, SrO and BaO

Molecule/state	$r_e(\text{\AA})^a$			$\omega_e(\text{cm}^{-1})^a$		
	SCF	CI(SD)	Expt ^b	SCF	CI(SD)	Expt ^b
BeO($^1\Pi$)	1.456	1.456	1.463	1180	1169	1144.24
MgO($^3\Pi$)	1.852	1.857	1.87	690	685	650
CaO($^3\Pi$)	2.105	2.087	2.09 ₉	561	542	556
SrO($^3\Pi$)	2.236	2.217	2.196	453	491	464
BaO($^3\Pi$)	2.347	-----	2.289	424	---	445.4

^aSpectroscopic parameters are based on a parabolic fit to the lowest energy points on a 0.1 Bohr grid.

^bValues taken from Huber and Herzberg [69].

Table XIII. Theoretical dissociation energies (D_o) and $^2\Pi - ^2\Sigma^+$ energy separations for the alkali sulfides Li-Rb

Molecule	D_o (eV) ^{a,b}	T_e (cm ⁻¹) for $A^2\Sigma^+$ ^b
LiS	3.19(3.22)	5107(5035)
NaS	2.50(2.66)	3814(4033)
KS	2.51(2.68)	1717(1827)
RbS	2.39(2.58)	1240(1280)

^aDissociation energies are for the $X^2\Pi$ states with respect to ground state atoms.
Zero-point corrections based on theoretical ω_e values in Table XIV.

^bThe SCF values are given first with CI(SD) values given in parentheses.

Table XIV. Theoretical spectroscopic parameters (r_e , ω_e) for the $X^2\Pi$ and $A^2\Sigma^+$ states of the alkali sulfides Li-Rb^a

Molecule	$r_e(\text{\AA})^b$		$\omega_e(\text{cm}^{-1})^b$	
	$X^2\Pi$	$A^2\Sigma^+$	$X^2\Pi$	$A^2\Sigma^+$
LiS	2.166(2.163)	2.100(2.093)	582(572)	538(536)
NaS	2.515(2.487)	2.454(2.424)	397(339)	326(319)
KS	2.890(2.843)	2.776(2.717)	223(239)	250(261)
RbS	3.036(2.983)	2.903(2.834)	208(214)	198(200)

^aSpectroscopic parameters are based on a parabolic fit to the lowest energy points on a 0.1 Bohr grid.

^bThe SCF values are given first with the CI(SD) values given in parentheses.

Table XV. Theoretical spectroscopic parameters (r_e , ω_e , D_e) for the $A^1\Pi$ states of BeS, MgS and CaS.^a

Molecule	$r_e(\text{\AA})$ ^b	$\omega_e(\text{cm}^{-1})$ ^b	D_e (eV) ^{b,c}	$a^3\Pi - A^1\Pi$ energy separation(cm^{-1}) ^b
BeS	1.926(1.921) ^d	796(784) ^d	2.04(2.29)	937(941)
MgS	2.335(2.310)	431(415)	1.49(1.70)	731(859)
CaS	2.643(2.601)	320(338)	2.24(2.41)	319(374)

^aThe $a^3\Pi$ r_e and ω_e values are not reported since they are essentially the same as those for the $A^1\Pi$ states.

^bThe SCF values are given first with the CI(SD) values in parentheses.

^cDissociation energies for the $A^1\Pi$ states (no zero-point correction) with respect to ground state atoms. To convert to ground state D_∞ , add $T_e(A^1\Pi)$ and subtract $X^1\Sigma^+$ zero-point energy.

^dExperimental values are $r_e=1.907$ and $\omega_e=762.46 \text{ cm}^{-1}$ from observation of the electronic spectrum by Cheetham et al [77].

Table XVI. Dissociation energies (D_o) of the alkali and alkaline-earth hydroxides

Molecule	Theoretical D_o (eV) ^a	Experimental D_o (eV)
LiOH	4.65(4.64)	4.55 ± 0.09^b , 4.64 ± 0.09^c , 4.54^d
NaOH	3.48(3.51)	3.47 ± 0.09^b , 3.38^d
KOH	3.49(3.59)	3.69 ± 0.09^b , 3.53^d
RbOH	3.43(3.54)	3.77 ± 0.09^b , 3.61^d
CsOH	3.57(3.71)	3.90 ± 0.09^b , 3.95^d
BeOH	4.64(4.70) ^e	5.51^f , 4.94 ± 0.43^g
MgOH	3.33(3.31)	4.16 ± 0.13^h , 2.43 ± 0.22^i , 3.59 ± 0.22^j 3.19 ± 0.22^k
CaOH	4.10(4.13)	4.44 ± 0.07^l , 4.51^m , 4.08 ± 0.13^n 4.00 ± 0.17^o
SrOH	4.11(4.16)	4.31 ± 0.10^p , 4.47^m , 4.03 ± 0.13^q 4.00 ± 0.17^o
BaOH	4.30(4.38)	4.64^r , 4.94^m , 4.73 ± 0.13^n 4.55 ± 0.17^o

^aSCF values are given first with CI(SD) values in parenthesis. We used the following zero-point corrections (eV) in converting our D_e values to D_o : LiOH(0.10), NaOH(0.08), KOH(0.07), RbOH(0.06), CsOH(0.06), BeOH(0.10), MgOH(0.07), CaOH(0.08), SrOH(0.08), and BaOH(0.08).

^bCotton and Jenkins(1969) [82], atomic absorption spectroscopy in flames .

^cZeegers and Alkemade(1970) [83], flame photometry.

^dJensen(1970) [84], flame photometry.

^eCalculation at linear geometry. Calculations with a smaller basis set show a bent geormetry to be about 0.01 eV more stable.

^fKo, Greenbaum and Farber(1967) [85], molecular flow effusion.

^gInami and Ju(1968) [86], flame photometry, as reported in JANAF 1978.

^hCotton and Jenkins(1969a) [88], flame photometry.

- ⁱBulewicz and Sugden(1959) [89], flame photometry.
- ^jEstimate from JANAF Tables(1978) [87].
- ^kMurad(1980) [90], mass spectrometry.
- ^lKalff and Alkemade(1973) [96], flame photometry.
- ^mCotton and Jenkins(1968) [92], atomic absorption spectroscopy in flames.
- ⁿRyabova, Khitrov and Gurvich(1972) [93], flame photometry.
- ^oMurad(1981) [94], mass spectrometry.
- ^pHurk, Hollander, and Alkemade(1974) [95], recalculation of work in footnote l.
- ^qGurvich, Ryabova, Khitrov, and Starovoitov(1971) [91], flame photometry.
- ^rStafford and Berkowitz(1964) [97], mass spectrometry.

**Table XVII. Theoretical spectroscopic parameters (r_e , ω_e)
for the ground states of the alkali and alkaline-earth hydroxides**

Molecule ^a	$r_e(\text{\AA})^b$			$\omega_e(\text{cm}^{-1})^b$		
	SCF	CI(SD)	Expt	SCF	CI(SD)	Expt
LiOH	1.576	1.573	1.58 ^c	941	931	
NaOH	1.940	1.932	1.95 ^d	588	579	431 ^e
KOH	2.235	2.208	2.196 ^f	455	467	408 ^g
RbOH	2.349	2.323	2.301 ^h	380	398	354 ^e
CsOH	2.448	2.419	2.391 ^h	350	378	400±80 ⁱ , 336 ^j
BeOH ^k	1.371	1.372 ^j	----	1340	1343	----
MgOH	1.757	1.758	----	810	802	----
CaOH	2.006	1.988	1.976 ^l	612	629	623 ^l
SrOH	2.134	2.117	2.10 ^m	547	533	522 ^m
BaOH	2.251	2.234	----	483	502	----

^aThe ground state is ${}^1\Sigma^+$ for the alkali hydroxides and ${}^2\Sigma^+$ for the alkaline-earth hydroxides.

^bThe metal-oxygen values assuming a rigid OH subunit with a fixed OH bond distance of 0.9472Å. The parameters are based on a parabolic fit to the lowest energy points on at least a 0.1 Bohr grid.

^cChase et. al. (1974) [78], computed using moment of inertia reported by Freund et. al., 25th Spectroscopy conference (Columbus, 1970) paper E8.

^dKuijpers, Torring and Dymanus(1976) [101], microwave.

^eAcquista and Abramowitz(1969) [102], matrix isolation.

^fPearson, Winnewisser and Trueblood(1976) [103].

^gBelyaeva, Dvorkin and Sheherba(1966) [104].

^hLide and Matsumura(1969) [105].

ⁱLide and Kuczkowski(1967) [106], gas phase.

^jAcquista, Abramowitz and Lide(1968) [107], matrix isolation.

^kComputed at the linear geometry. Calculations with a smaller basis yield a bent structure at the SCF(CI) level of R(Be-O)=1.390Å (1.396Å), R(O-H)=0.933Å (0.948Å), and $\theta=34^\circ$ (33°).

^lHilborn, Qingshi, and Harris(1983) [108], gas phase.

in Nakagawa, Wormsbecher and Harris(1983) [109], gas phase.

**Table XVIII. Theoretical dissociation energies for some
alkaline-earth (iso)cyanides**

Molecule	dissociation energies(eV) ^a			
	Cyanide	Bmp ^b	Isocyanide	Expt ^c
BeCN	3.62(3.83)	3.17(3.38)	4.10(4.09)	4.46±0.29
MgCN	3.07(3.22)	3.00(3.12)	3.36(3.35)	4.21±0.26
CaCN	3.78(3.89)	3.88(3.96)	4.12(4.09)	4.46±0.22
BaCN	4.02(-----)	4.17(-----)	4.34(4.33)	4.87±0.26

^aDissociation energies (without zero-point corrections) relative to CN($^2\Sigma^+$) + M(1S). SCF values are given first with CI(SD) values in parentheses.

^bThe metal atom is approaching the CN bond mid point.

^cL'vov and Pelieva(1980) [118], electrothermal atomic absorption spectrometry.

Table XIX. Recommended dissociation energies (D_o) for selected alkali and alkaline-earth fluorides, chlorides, oxides, sulfides, hydroxides and isocyanides.

Molecule	State	D_o (eV)	Molecule	State	D_o (eV)
LiF	$^1\Sigma^+$	6.06	BeF	$^2\Sigma^+$	5.94
NaF	$^1\Sigma^+$	5.00	MgF	$^2\Sigma^+$	4.68
KF	$^1\Sigma^+$	5.10	CaF	$^2\Sigma^+$	5.53
RbF	$^1\Sigma^+$	5.07	SrF	$^2\Sigma^+$	5.62
CsF	$^1\Sigma^+$	5.27			
LiCl	$^1\Sigma^+$	4.89	BeCl	$^2\Sigma^+$	3.90
NaCl	$^1\Sigma^+$	4.22	MgCl	$^2\Sigma^+$	3.26
KCl	$^1\Sigma^+$	4.37	CaCl	$^2\Sigma^+$	4.14
RbCl	$^1\Sigma^+$	4.36	SrCl	$^2\Sigma^+$	4.23
CsCl	$^1\Sigma^+$	4.58			
LiO	$^2\Pi$	3.84	BeO	$^1\Sigma^+$	4.69
NaO	$^2\Pi$	2.83	MgO	$^1\Sigma^+$	2.75
KO	$^2\Sigma^+$	2.86	CaO	$^1\Sigma^+$	4.14
RbO	$^2\Sigma^+$	2.90	SrO	$^1\Sigma^+$	4.36
CsO	$^2\Sigma^+$	3.10	BaO	$^1\Sigma^+$	5.75
LiS	$^2\Pi$	3.30	BeS ^a	$^1\Pi$	2.29
NaS	$^2\Pi$	2.67	MgS ^a	$^1\Pi$	1.70
KS	$^2\Pi$	2.74	CaS ^a	$^1\Pi$	2.41
RbS	$^2\Pi$	2.66			
LiOH	$^1\Sigma^+$	4.64	BeOH	$^2\Sigma^+$	4.70
NaOH	$^1\Sigma^+$	3.51	MgOH	$^2\Sigma^+$	3.31
KOH	$^1\Sigma^+$	3.61	CaOH	$^2\Sigma^+$	4.15
RbOH	$^1\Sigma^+$	3.58	SrOH ^b	$^2\Sigma^+$	4.18
CsOH	$^1\Sigma^+$	3.77	BaOH ^b	$^2\Sigma^+$	4.60
			BeNC	$^2\Sigma^+$	4.15
			MgNC	$^2\Sigma^+$	3.37

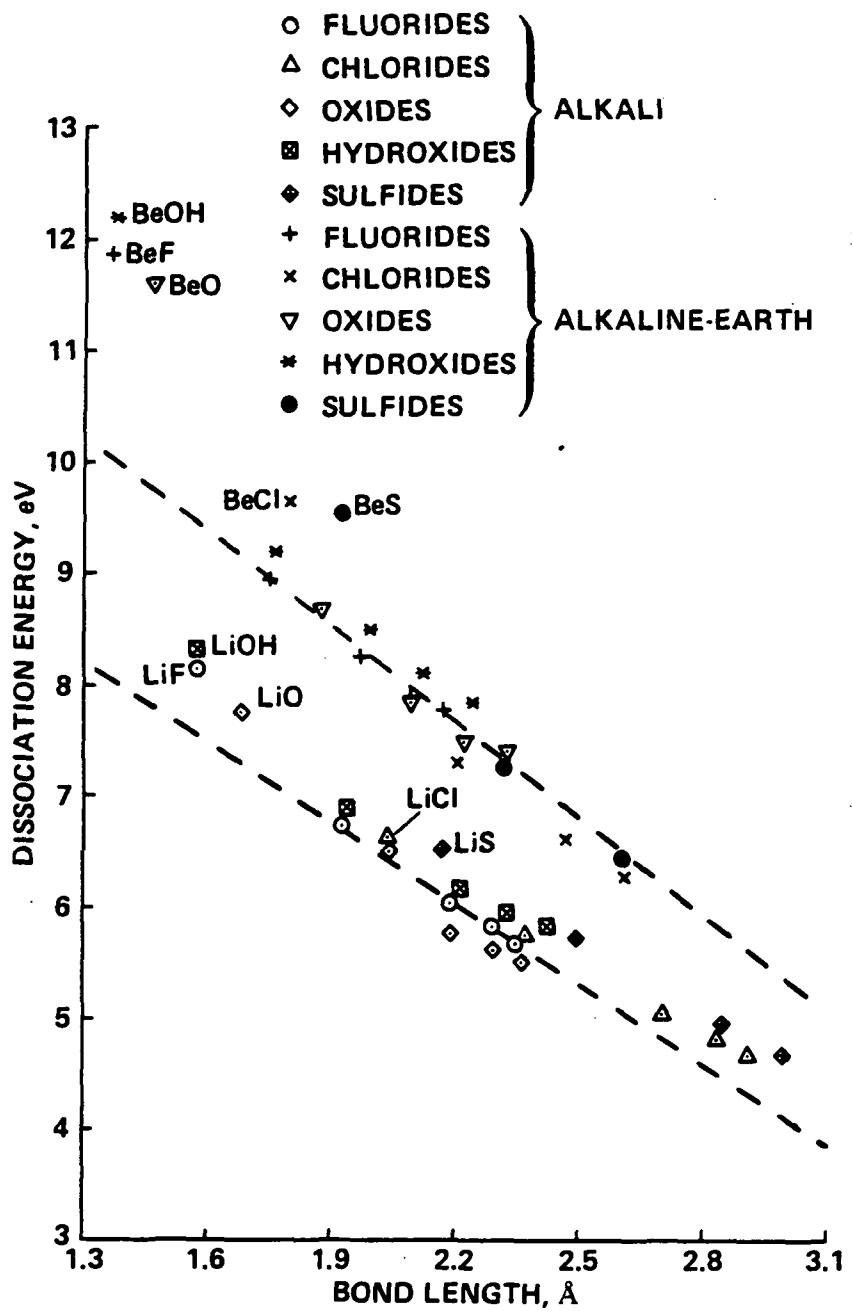
CaNC	$^2\Sigma^+$	4.13
BaNC ^b	$^2\Sigma^+$	4.50

^aThe dissociation energy (D_e) reported is for the excited $A^1\Pi$ state and does not include a zero-point correction (see Table XV).

^bThe results are less accurate (≈ 0.2 eV uncertainty) because the core electrons are described by a relativistic effective core potential (see text).

Figure caption

Figure 1. The dissociation energy (without zero point corrections) with respect to the ionic limits versus bondlength.





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